

COKING OF COAL SOLUTIONS IN A LABORATORY COKE OVEN

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INTRODUCTION

The manufacture of aluminum by the Hall-Heroult process requires nearly one-half pound of high-grade carbon for each pound of aluminum produced. This carbon must contain a minimum of metallic impurities to prevent contamination of the aluminum produced in the process. For this reason raw materials used in the anode manufacture for the aluminum industry have stringent purity specifications. Petroleum coke represents a large volume source of relatively pure carbon and is used extensively throughout the aluminum industry as the material of choice for anode manufacture.

Most of the petroleum coke that is used in electrode manufacture is produced in delayed cokers where the product is subsequently calcined in rotary kilns to temperatures of 1200°C — 1430°C ¹. After heat treatment to this temperature the coke has obtained dimensional stability and electrical conductivity suitable for its use as an electrode material. Coke produced by this process usually has a particle size adequate for its use in the manufacture of large monolithic electrodes. A limited amount of petroleum coke produced in fluid bed cokers is used in the manufacture of anodes for the aluminum process. Fluid coke is sometimes used as a supplement to delayed petroleum coke to produce electrodes. The absence of large size particles in fluid coke generally limit its use in large electrodes. A limited amount of coke is produced for electrode use by the delayed coking of Gilsonite². Recently, the Nittetsu Chemical Industry of Japan completed the installation of a delayed coker for the coking of coal tar pitch for electrode use^{3,4}. Some coal tar pitch coke is manufactured in Europe to supplement the supply of petroleum coke. This coke is generally produced in coke ovens⁵.

Coke derived from coal had not been used as a general source of anode carbon in alumina reduction cells because of its high ash content. Investigators have studied methods of removing mineral matter from coal,⁶⁻¹¹ and coke from purified coal has been used on a commercial scale in at least two cases¹²⁻¹⁴. These were war-time uses that were discontinued when adequate supplies of high-grade petroleum coke were available.

Because of possible future shortages of electrode grade petroleum coke, we have studied the coking of purified solutions of coal in creosote oil as a process for producing an alternate source of electrode grade coke. A pilot plant was constructed at Reduction Research Laboratory where high-volatile bituminous coal was mixed with heavy residue creosote oil and digested under pressure to give a solution of coal. The solution was treated with a combination

of disc and solid bowl centrifuges to yield a solution of coal that had been freed from its mineral matter and fusain. Most of the solvent oil was removed from the coal by distillation in a continuous still and the pitch-like residue remaining from the distillation was charged as a liquid to a coke oven where the remaining solvent and volatile matter were removed to produce a calcined electrode grade coke¹⁵. The principal process steps are shown diagrammatically in Figure 1. This paper will be concerned primarily with our experience in operating a laboratory coke oven to produce calcined coke.

While much excellent work has been published on the solubility of coal in different solvents¹⁵⁻²³, little has been published about coking of such solutions to yield coke. We were aware that most of the petroleum coke was produced in delayed cokers and that Gilsonite was being coked in delayed cokers to produce a high-grade electrode coke, but we were uncertain that a product as aromatic as dissolved coal could be satisfactorily handled in a delayed coker. The Koppers Company in the United States had coked coal tar pitch in coke ovens; coke ovens are being used to coke coal tar pitch in Russia²⁴ and Germany; and we were aware that the coal solution produced in the Pott-Broche process in Germany during World War II had been coked in slot ovens¹³.

The product of a delayed coker is not satisfactory for use in an alumina reduction cell without further heat treatment to remove the residual volatile matter, obtain proper electrical conductivity, and insure dimensional stability of the coke particles at high temperature. Generally, the coke from the delayed coker is heat treated or calcined to a temperature of about 1300°C before use in alumina reduction cell anodes. Thus, the use of a delayed coker would also require the use of a calciner. We elected to combine the two steps in our pilot plant and construct the only coker that we knew of capable of operating at temperatures of 1300°C - the coke oven.

PROCESS DESCRIPTION

The Bureau of Mines had reported²⁵ on a coke oven heated with silicon carbide glow bars of the approximate size that we needed. We used the general idea of this coke oven as our model, with the exception that the coke oven we constructed was gas fired and the sole of the oven was heated by the passage of hot gas from the flue to the exhaust stack. The oven was fired symmetrically with burners at four corners of the flues, and the flues were baffled to provide uniform heat distribution for the entire surface of the refractory. The coking slot was 17 inches wide by 48 inches long by 48 inches high and was tapered one-quarter inch from the pusher end to the coke end over the length of the slot. The slot walls were silica refractory of the type used in commercial coke ovens while the sole was super-duty fire-clay refractory. The roof and doors were cast with super-duty castable refractory. Tongue and groove construction was used to maintain better seals in the refractory joints. The oven was fired with four 158,000 Btu per hour capacity gas burners. The system was protected against high and low gas pressure and blower failure. Because the refractories were incandescent during operation, flame failure protection was regarded as superfluous. Figures 2 and 3 are diagrammatic sections through the coke oven.

Cokes from the solution of two different coals were studied in the coke oven. Both of these coals were high volatile bituminous coals. One was the Black Creek Seam in Northern Alabama and the other, the No. 9 Seam in Western Kentucky. Typical analysis of these coals are shown in Table I. Prior to each charging, the door faces were cleaned, seated on a strand of asbestos rope and sealed with a refractory cement.

Steam was introduced into the oven slot to reduce the surface temperature of the refractories before charging the dissolved coal to the oven. This was done to minimize the amount of carbon-black formed by cracking of the coal solution on the incandescent refractory surfaces. After passing through the continuous still where part of the solvent was removed by distillation, the dissolved coal solution was fed into the top of the coking slot and the volatile matter and gases that were flash evaporated were passed through a condenser. The condensed vapor was collected in a solvent recovery tank where it was recombined with the solvent fractions removed by the continuous still.

The hot coal solution was charged at a rate of about 2 — 3 gallons per minute into the slot of the coke oven. While this material left the still at about 320°C, it had cooled to about 200°C in the piping by the time it had reached the coke oven. During the first few minutes of the charge the condenser was flushed with a spray of water to wash away the copious quantities of carbon-black that were generated. When the first condensation of oil was observed, the water spray was discontinued in the condenser, and the condensing oil was turned into the solvent recovery tank. At this point the flow rate was reduced to about 1 gallon per minute. At a predetermined volume, usually 300 gallons, the feed rate to the coke oven was decreased to about 0.5 gallon per minute for the remainder of the usual 400 gallon charge. At that point the coke oven was removed from the feed circuit and the lines and still were flushed with recovered oil. The oven was observed for about one hour after the completion of the charge for excessive frothing.

Malfunctions in the operation, such as oven door leakage or excess oven pressure, were corrected as they occurred. If care was taken to clean the condenser and prevent excess pressure from developing in the oven, the carbon-black formed at the beginning of the charge soon sealed the doors and cracks in the flues, and the operation settled down to a relatively smoke-free condition. Figure 4 illustrates typical temperature cycles during the operation of the coke oven.

After completion of the charge, the coke was held in the oven for an additional 8 — 10 hours to permit the coke to obtain a uniform temperature of 1250°C — 1300°C. This temperature was measured with an optical pyrometer on the coke surface through an observation port in the top of the furnace. Before any work was done on the oven, a valve was closed between the condenser and the receiver tank. This was done to prevent hot gases and sparks from the oven from igniting any accumulated combustible gases in the tank.

At the completion of the coking cycle, the doors were lifted and the coke was pushed from the oven with a mechanical ram. During pushing the coke was quenched slightly with water and permitted to evaporate to dryness. As removed from the oven the coke was in large strong, angular lumps with some anisotropic

structure. Properties of the cokes compared with that of a typical petroleum coke are shown in Table II. Use of the coke in anodes of commercial reduction cells showed the coke to be satisfactory in every respect²⁶.

DISCUSSION

As the gases from the coke oven were vented to the atmosphere and the liquid product recombined with the solvent oil removed by distillation, it was not practical to obtain a material balance on the coking operation. However, work done by the Bureau of Mines from the coking of the Black Creek coal in retorts at 1000°²⁷ provides some insight into the product distribution that could be expected from this coal on carbonization. This information is shown in Table III along with the coke yield from a series of coke oven runs involving some 20 tons of coal from the Black Creek Seam. About 44 percent of the original coal is converted to calcined coke that would be usable in aluminum cell anodes. The coke obtained from coking the purified coal solution, when combined with the coke obtained from coking the centrifuge sludge, agrees within about 2 percent of the amount of coke predicted by the Bureau of Mines for this particular coal. This would indicate that the molecular size distribution of the coal has not been greatly altered by solution.

Normally, when we open the coke oven doors, we found that the coke charge had shrunk and pulled away from the coke oven walls. The charge could be pushed from the oven with very little effort. In some cases when it was necessary to interrupt the charge to the coke oven for any prolonged length of time (two hours) we found that the coke charge was stuck tightly to the oven wall and we were unable to remove the coke with the pusher. In these cases it was necessary to break the coke from the oven with steel bars. We adopted the practice of charging the solution to the oven continuously and if we were forced to interrupt our charge sequence for more than an hour we terminated the charge at that point and coked a partially filled oven.

Our experience has shown that we can produce a satisfactory electrode coke from high-volatile bituminous coal through a solution process followed by coking in a slot-type coke oven.

ACKNOWLEDGMENT

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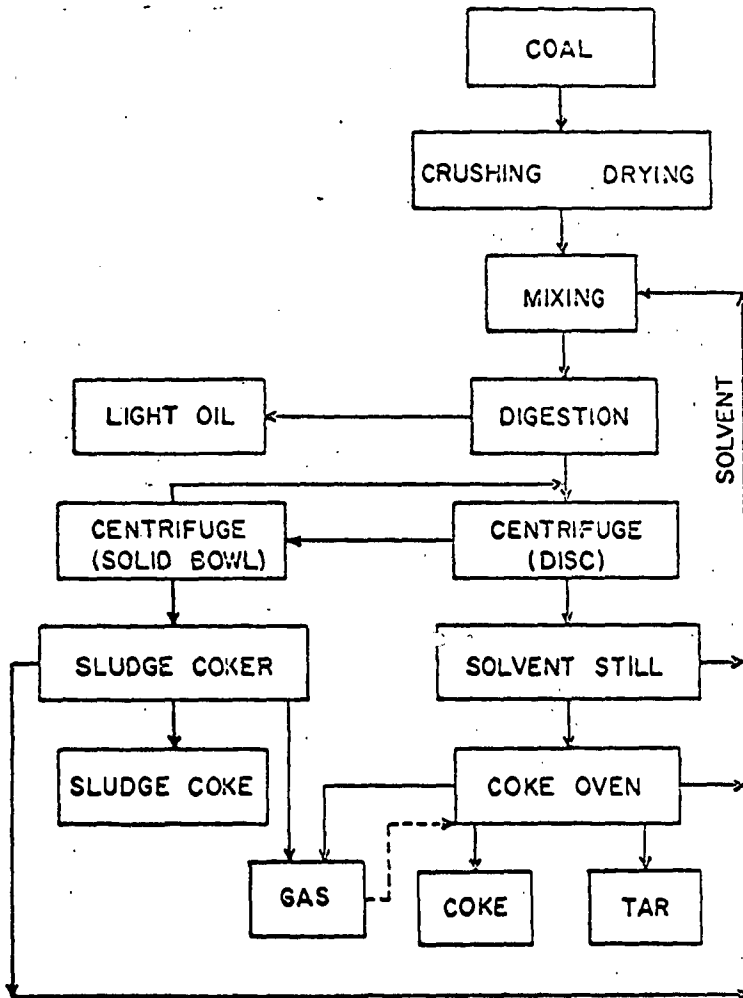


FIGURE 1. DIAGRAM OF A COKE-FROM-COAL PROCESS

TABLE I.
ANALYSES OF COALS USED IN INVESTIGATION
OF ELECTRODE COKE FROM COAL

	Black Creek Coal Seam		Kentucky No. 9 Coal Seam	
	As Received	Dry, Ash-Free	As Received	Dry, Ash-Free
Moisture	2.7	----	----	----
V. M.	35.4	37.4	40.5	45.0
Ash	2.8	----	9.9	----
H ₂	5.4	5.4	5.1	5.6
C	79.8	84.4	72.5	80.5
N ₂	1.7	1.8	1.5	1.7
O ₂	9.5	7.6	7.9	8.8
S	.8	.8	3.1	3.4
Anthraxylon		45		65
Trans. Attritus		38		27
Opaque Attritus		7		5
Fusain		10		3
B. t. u.	14,310	15,150	13,060	14,500

Source: Bureau of Mines. Bull. 550.

TABLE II.

PROPERTIES OF COKES FROM KENTUCKY COAL AND
ALABAMA COAL AFTER CALCINING TO 1340°C

	Alabama Coke	Kentucky Coke	Typical Petroleum Coke
Specific Gravity	2.02	2.01	2.03
Electrical Resistivity, ohm-in.	0.029	0.034	0.034
Hardgrove Grindability Index	22	22.5	37
Sulfur, Percent	0.46	0.67	0.8 - 1.65
Silicon, Percent	0.04	0.09	0.03
Iron, Percent	0.07	0.08	0.05
Aluminum, Percent	0.09	0.09	0.02
Ash, Percent	0.58	0.76	0.34

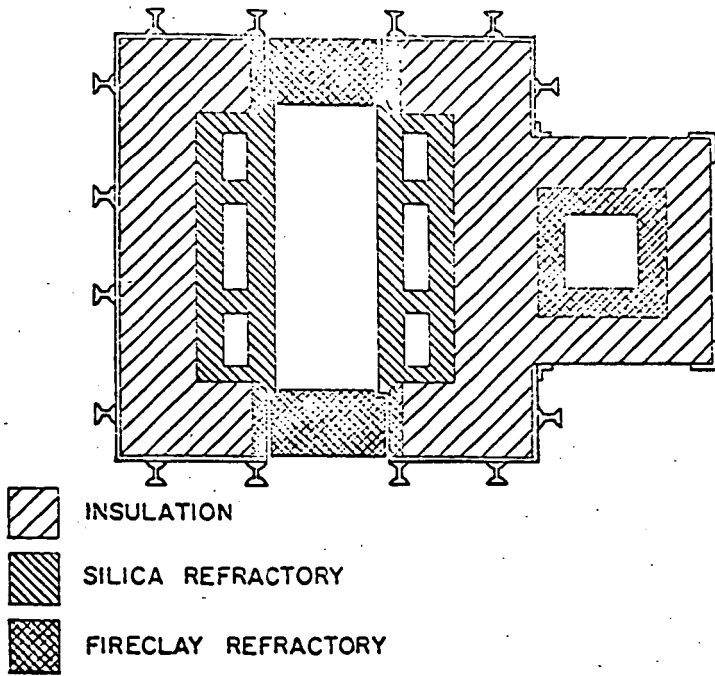


FIGURE 2. EXPERIMENTAL COKE OVEN TYPICAL CROSS SECTION THROUGH FLUES AND COKE CHAMBER (VIEWED FROM ABOVE)

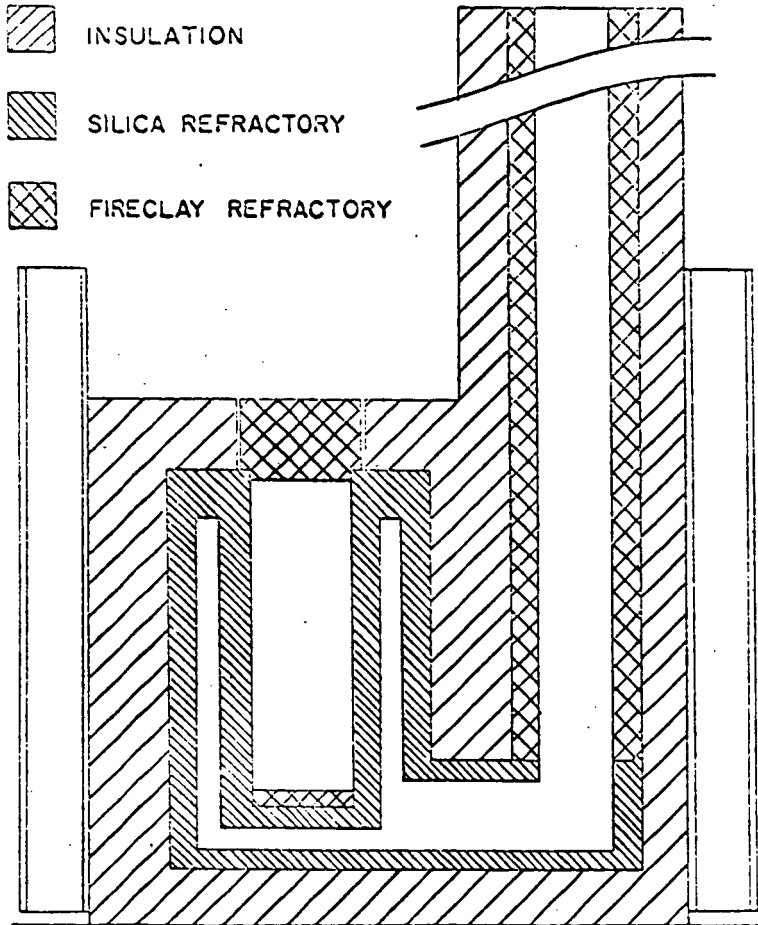


FIGURE 3. EXPERIMENTAL COKE OVEN - TYPICAL CROSS SECTION THROUGH FLUES AND COKE CHAMBER (VIEWED FROM COKE END)

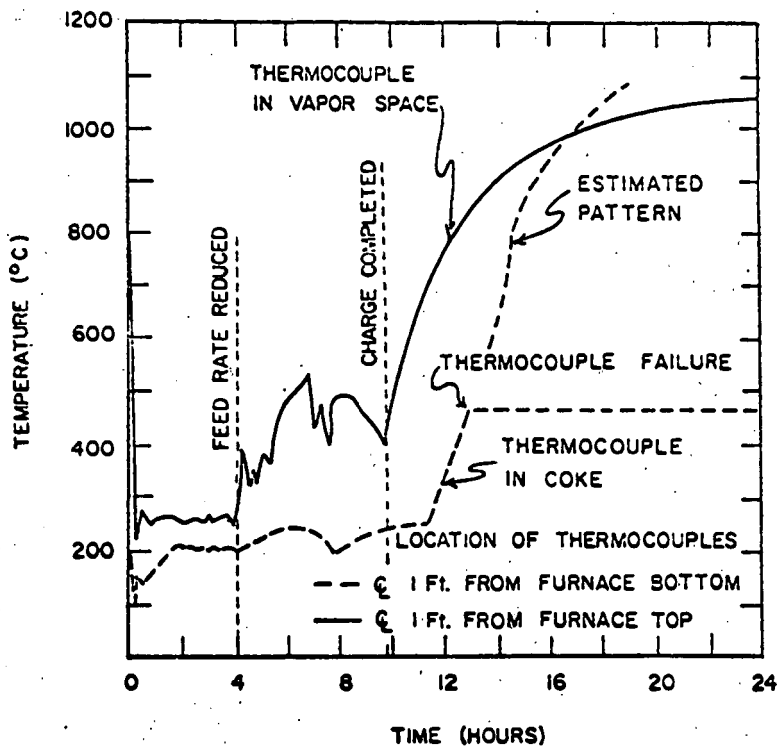


FIGURE 4. TEMPERATURE PATTERN IN COKE SLOT DURING COKING

TABLE III.
PRODUCT YIELD FROM COKING OF
BLACK CREEK COAL

	Estimated ¹	Found
COKE	66.6%	44.2%
CENTRIFUGE RESIDUE COKE	----	24.4%
GAS	17.6%	----
TAR LIQUOR	6.7%	----
AMMONIA	0.2%	----
TAR	6.0%	----
LIGHT OIL	1.3%	----

¹Fieldner, A. C., et. al., Bureau of Mines Technical Paper 531, 1932.